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NATIONAL LABORATORY

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CLEERS Passive NO_x Adsorber (PNA)

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PACIFIC NORTHWEST NATIONAL LABORATORY

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Timeline

- ▶ Status: On-going core R&D

Budget

- ▶ FY18 funding – \$400K

Barriers and Technical Targets

- ▶ Emission controls contribute to durability, cost and fuel penalties
 - Low-temp performance is now of particular concern
- ▶ Improvements limited by:
 - Available modeling tools
 - Chemistry fundamentals
 - Knowledge of material behavior
- ▶ Effective dissemination of information

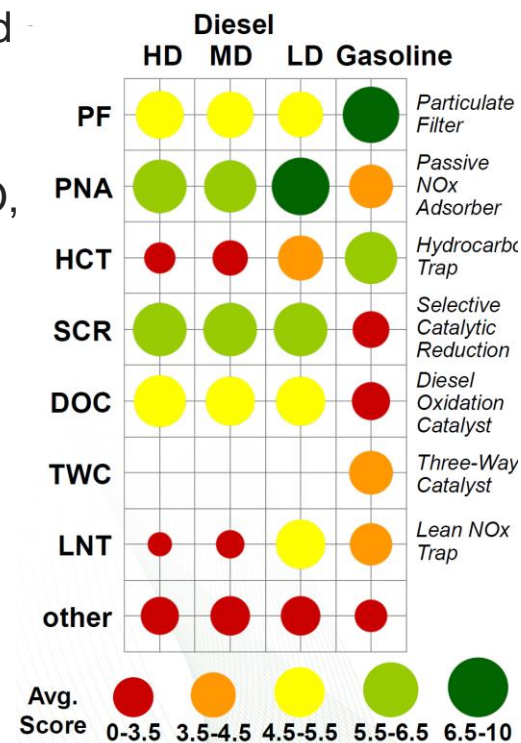
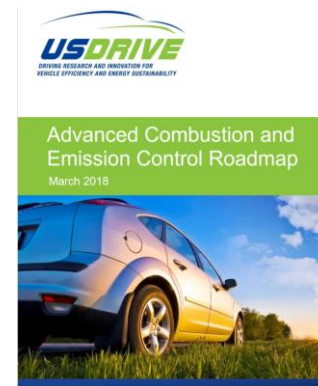
Partners

- ▶ Oak Ridge National Lab: synergies in evaluating both practical and model materials
- ▶ BASF: focus on addressing industrially relevant issues



Relevance

- ▶ Increasing the efficiency of internal combustion engines is a technologically-proven and cost-effective approach to dramatically improving the fuel economy of the nation's fleet of vehicles in the near- to mid-term, with the corresponding benefits of reducing our dependence on foreign oil and reducing carbon emissions.
- ▶ The overarching emissions goal is the U.S. EPA Tier 3 Bin 30 emission standard.
- ▶ Compliance with exhaust emission regulations will be mandated and requires aftertreatment technologies integrated with the engine combustion approaches.
- ▶ Achieve greater than 90% conversion of criteria pollutants (NO_x , CO, HCs) at 150°C for the full useful life of the vehicle (defined as the longer of 150,000 miles or 15 years).
- ▶ Require the research and development of new and novel material combinations that will enable lower temperature catalytic performance, increased selectivity to inert species, and optimal storage of pollutant and reductant species.
- ▶ Aligns with the 2017 CLEERS Industry Priorities Survey.



Relevance (and Goals)

- ▶ “CLEERS is a R&D focus project of the Diesel Cross-Cut Team. The overall objective is to promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems.”

CLEERS PNNL Subprogram Goal

Working closely with our National Lab partners, the CLEERS industrial/academic team and in coordination with our CRADA portfolio, PNNL will...

...provide the practical & scientific understanding and analytical base, e.g., *molecular level understanding of active sites*, required to enable the development of efficient, commercially viable emissions control solutions and *accurate modeling tools* for ultra high efficiency vehicles.

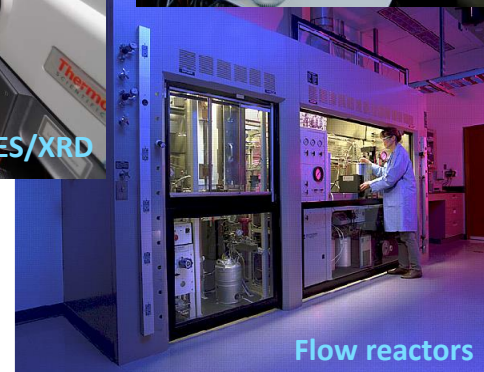
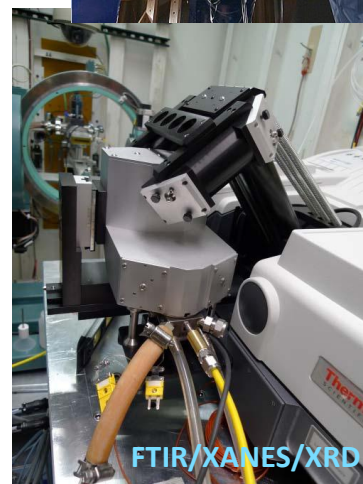
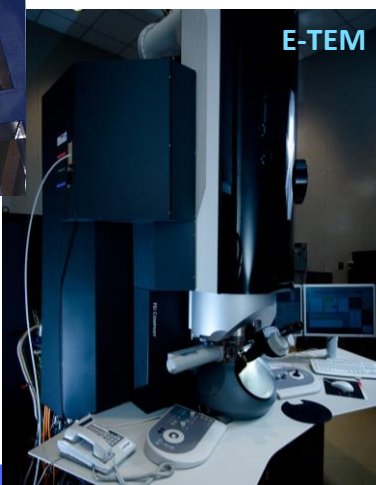
- ▶ VT program goals are achieved through these project objectives:
 - interact with technical community to identify relevant technological gaps
 - understand fundamental underlying mechanisms and material behavior
 - develop analytical and modeling tools, methodologies, and best practices
 - apply knowledge and tools to advance technologies leading to reducing vehicle emissions while improving efficiency
- ▶ Specific work tasks in support of the objectives are arrived at through:
 - focus group industrial monthly teleconferences, diesel cross-cut meetings
 - yearly workshops and surveys
 - ongoing discussions on program priorities with the VT office

Milestones:

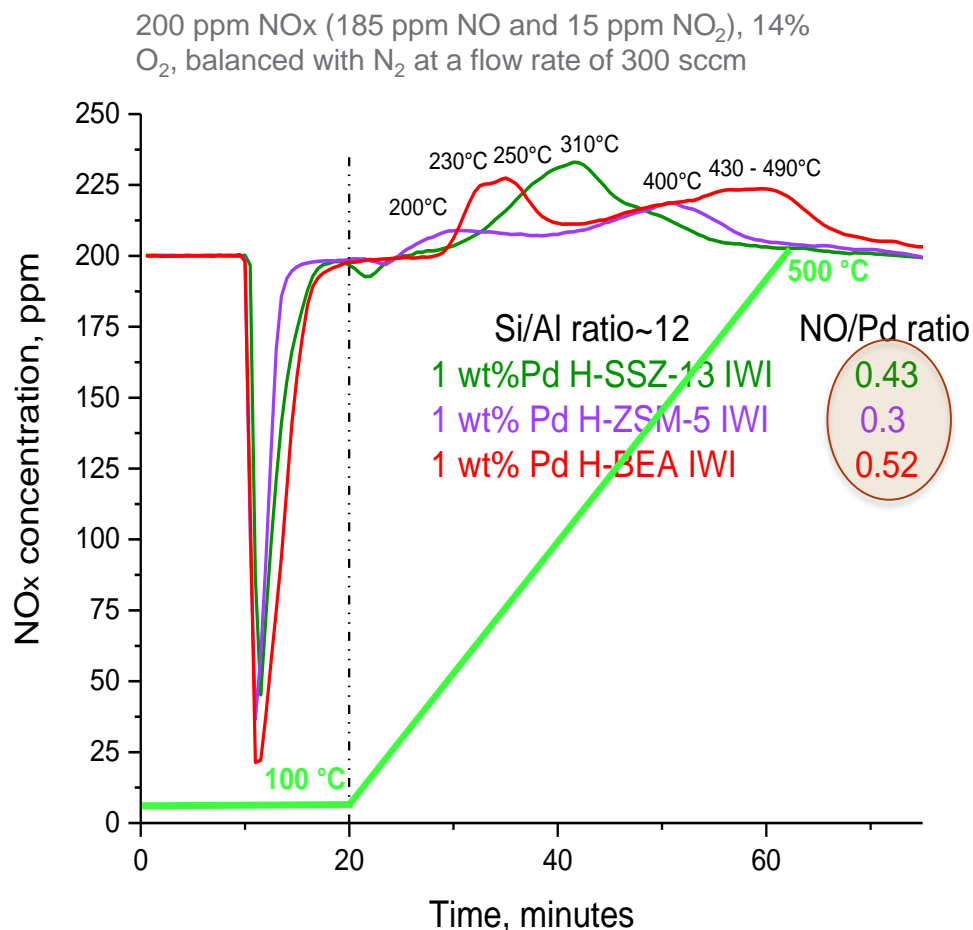
- | | | |
|---|-----------|----------|
| ▶ Achieve atomic dispersion of Pd by optimizing the preparation method and quantifying the dispersion of Pd species. | 3/31/2019 | ✓ |
| ▶ Provide molecular level understanding of the nature of active sites under practical conditions, e.g., CO, NO _x , H ₂ O, HCs | 7/30/2019 | on track |
| ▶ Identify the major cause of PNA material degradation associated with hydrothermal aging, cycling, and sulfur poisoning | 9/30/2019 | on track |
| ▶ Demonstrate >95% NO _x adsorption within 3mins at 100° C and release at >200° C (go/no-go decision) | 9/30/2019 | ✓ |

“Science to Solutions”

- ▶ Build on our strong base in fundamental sciences to reveal fundamental aspects of the chemistry and catalytic materials in PNA:
 - Institute for Integrated Catalysis (IIC)
 - Environmental Molecular Sciences Laboratory (EMSL)
 - Synchrotron Facilities
- ▶ Work closely with our partners and sponsors
 - ORNL (coordination of CLEERS Workshop, synergy in PNA, etc.)
 - BASF (addressing the issues of most importance to industries)

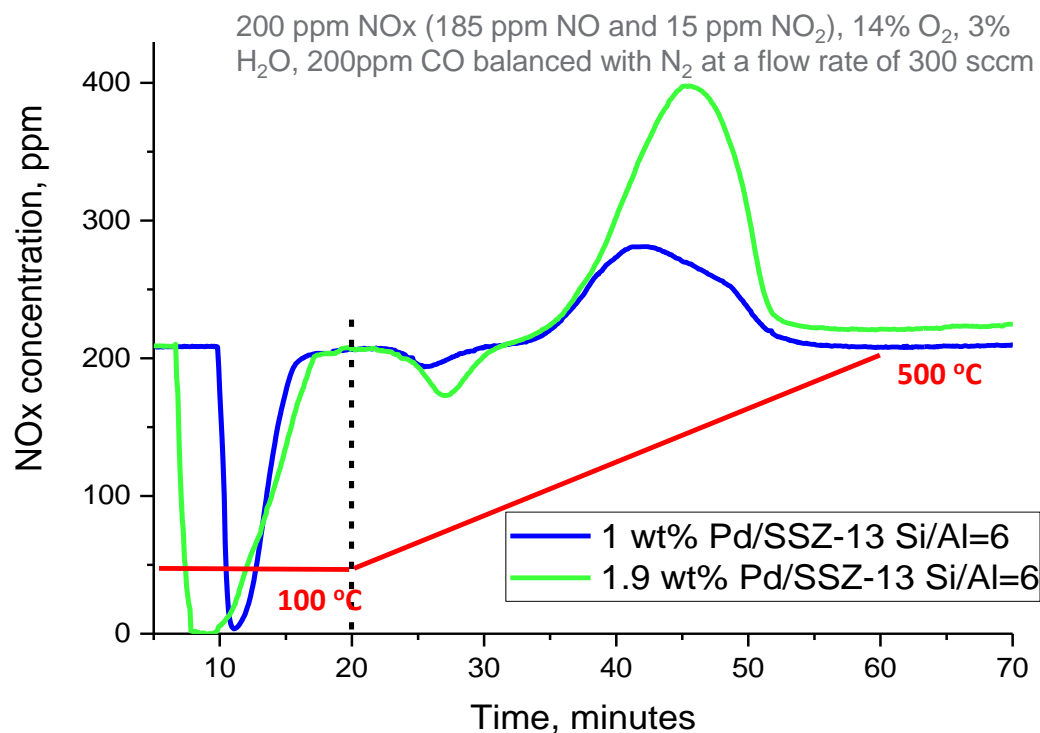


NO_x Adsorption and Release Depend on Zeolite Structure and Pd is Under-utilized

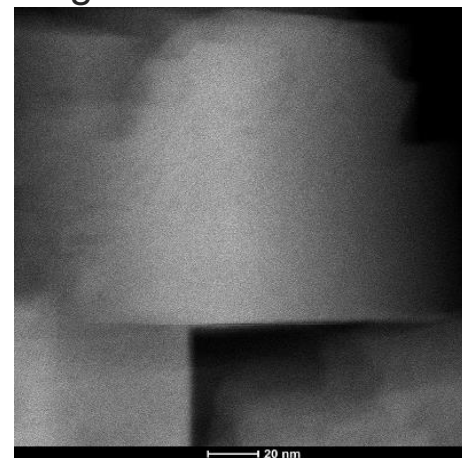


- ▶ Pd/Zeolite materials are active for PNA.
- ▶ Pd/BEA and Pd/SSZ-13 are the focus of studies - more active than Pd/MFI, BEA and SSSZ-13 are also the most stable ones for commercial use.
- ▶ Pd-SSZ-13 has the appropriate release temperature
- ▶ Effectiveness expressed as NO/Pd, Pd is underutilized and thus not used with maximum efficiency if <1.
- ▶ Pd utilization efficiency is far from ideal in Pd/Zeolite materials prepared by the traditional IWI method.

Preparation Route, Si/Al Ratio and Form of Zeolite are Critical: Achieving ~8 mg NO_x/g-catalyst Storage at NO/Pd of 0.9 with 3 wt% Pd/(NH₄)-SSZ-13 (Si/Al=6)



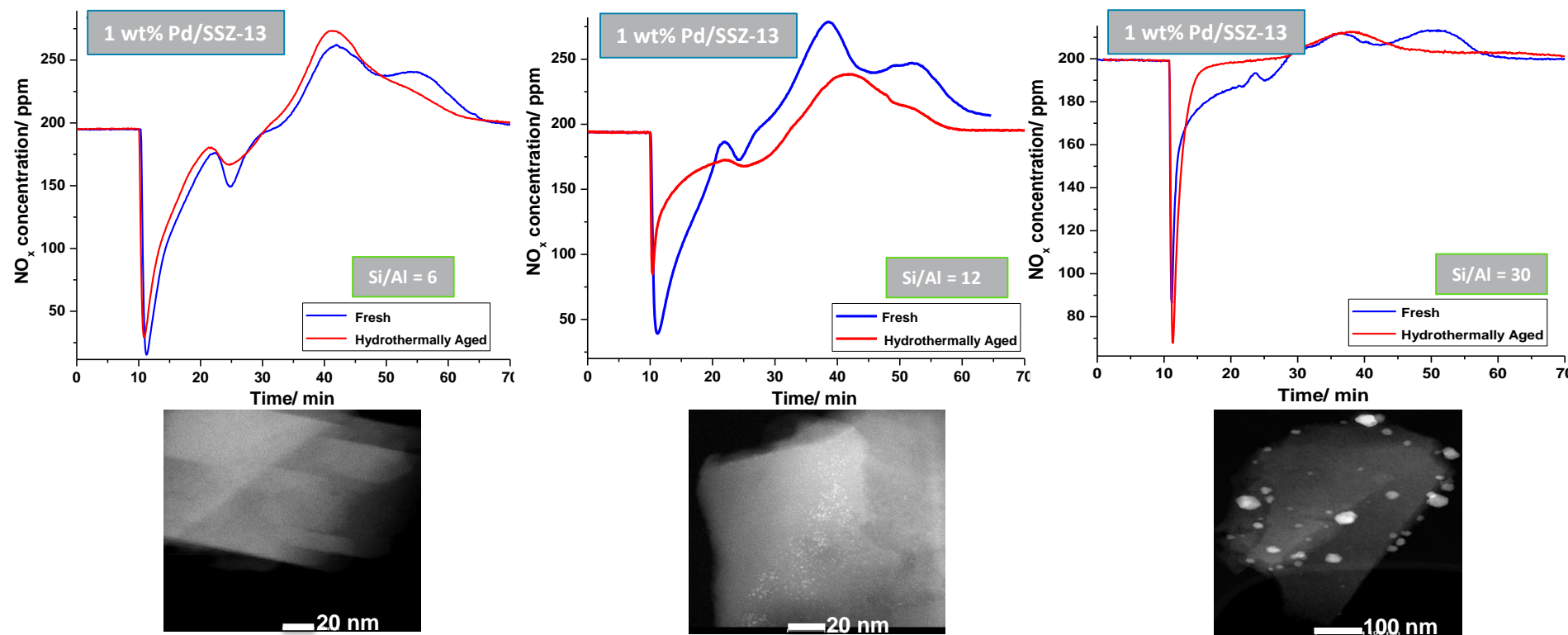
- ▶ Modified IWI preparation provides high performance PNA (Pd/Zeolite) materials.
- ▶ At Si/Al=6, atomic Pd dispersion is achieved at up to 2 wt% metal loading.
- ▶ Complete NO_x removal for ~3 min at 2 wt% Pd loading.
- ▶ At Pd loadings >2 wt%, Pd utilization efficiency decreases with metal loading.



Pd wt% (Si/Al 6)

	1	1.9	3	5
NO/Pd:	1	1	0.9	0.6
Storage (mg/g)	2.8	5.4	7.6	8.4

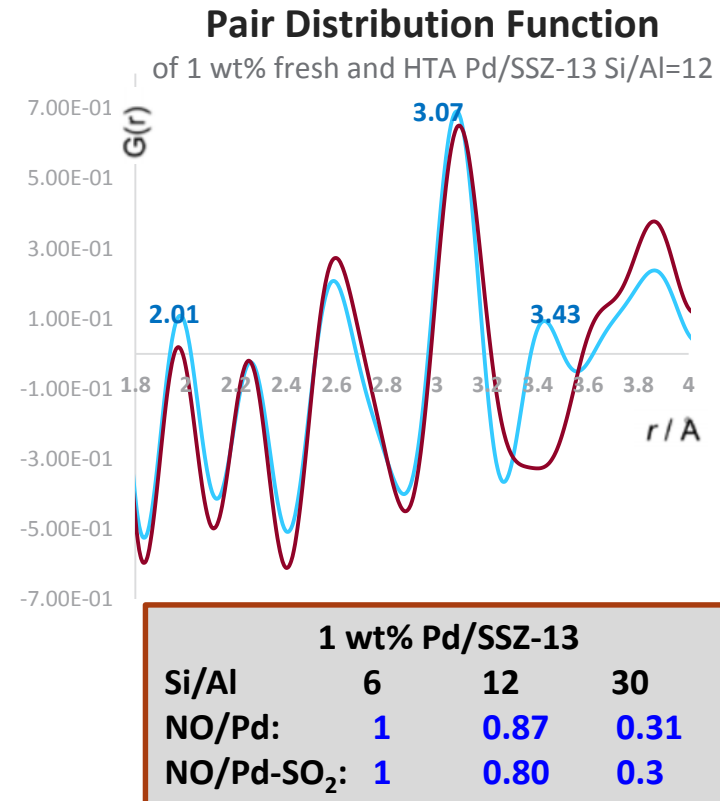
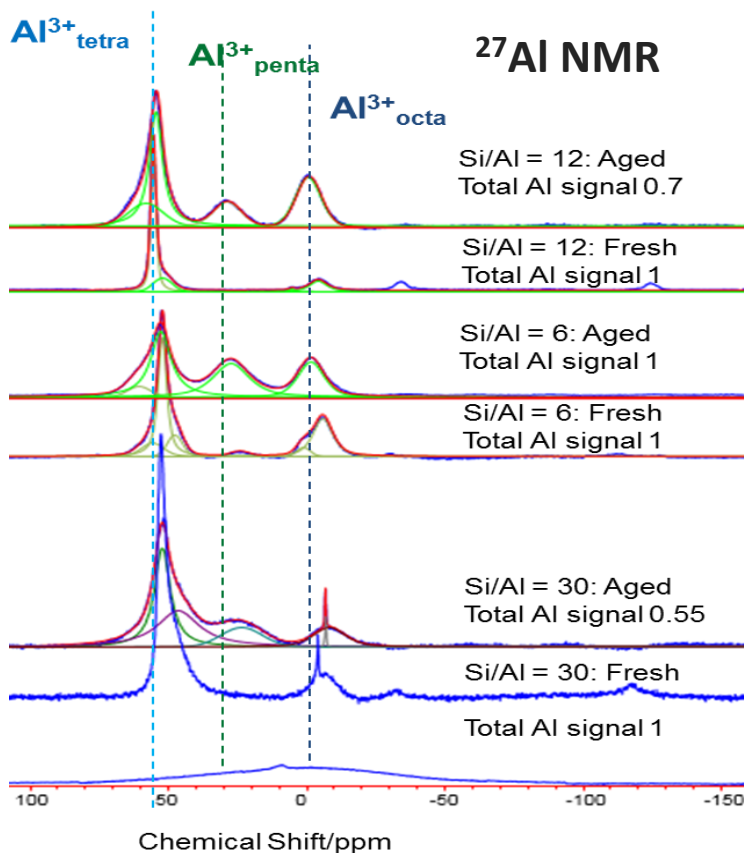
Atomically Dispersed Pd, e.g., 1wt%Pd/SSZ-13 Shows Better Hydrothermal Stability



Hydrothermal aging conditions: 750 °C in flowing air containing 10% water vapor for 16 hours.

- ▶ HTA reduces NO_x storage efficiency and affects the release temperature.
- ▶ HTA reduces or removes the high-temperature NO₂ desorption stage.
- ▶ Less than 10 to 20% performance lost for Pd/SSZ-13 (1-3 wt%Pd, Si/Al=6) with atomically dispersed Pd.

Hydrothermal Aging Leads to Dealumination of SSZ-13 and Negligible Sulfur Effect on 1wt% Pd/SSZ-13

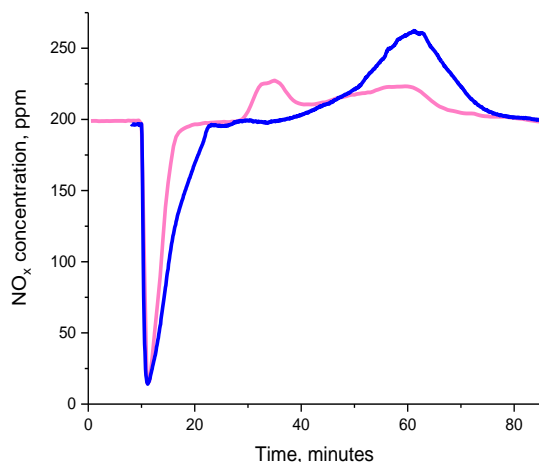


(The samples were treated using standard protocol:
5 ppm SO₂ in SO₂/10%O₂/N₂ mix for 5 hours at 300 °C)

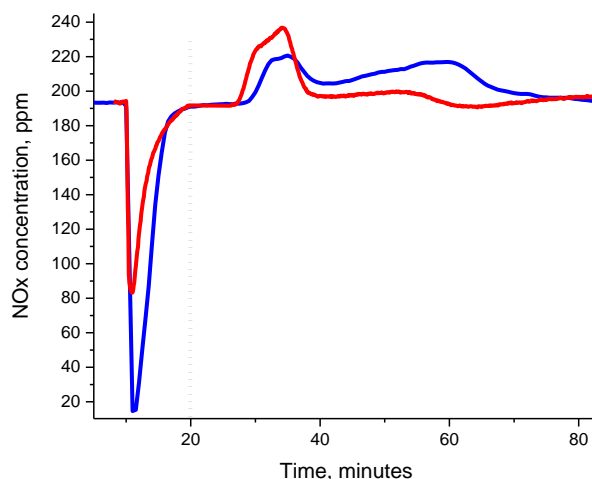
- ▶ After HTA, a large number of $\text{Al}^{3+}_{\text{penta}}$ ions form on both materials (Si/Al=6 and 12), and the $\text{Al}^{3+}_{\text{tetra}}$ ^{27}Al NMR signal broadens, possible due to the significant changes in the environment around these ions.
- ▶ Removal of framework Al ions (key in stabilizing isolated Pd ions) leads to the formation of PdO particles.
- ▶ Only minor performance degradation after SO₂ poisoning under the conditions studied.

Pd/BEA with Large Crystalline Size Shows Promising Hydrothermal Stability (1 wt% Pd/BEA)

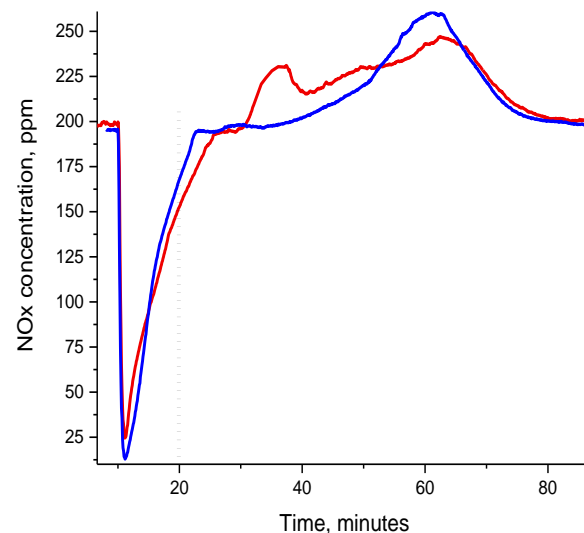
Fresh **nano** vs **large** BEA



Fresh vs **aged** nano BEA



Fresh vs **aged** large BEA

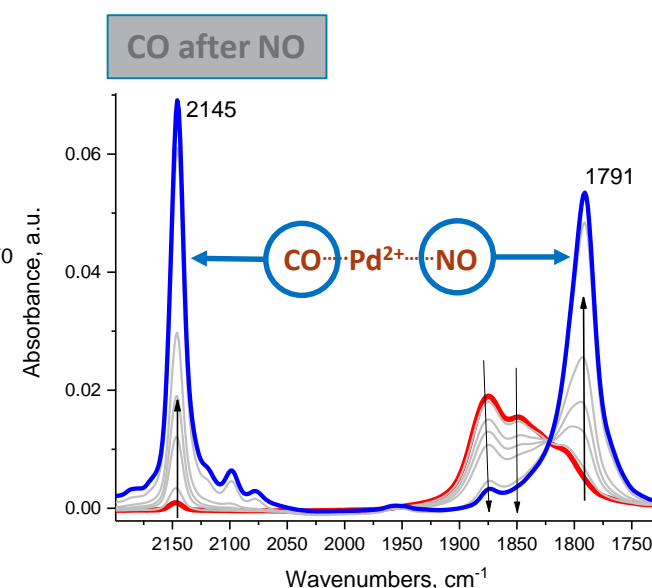
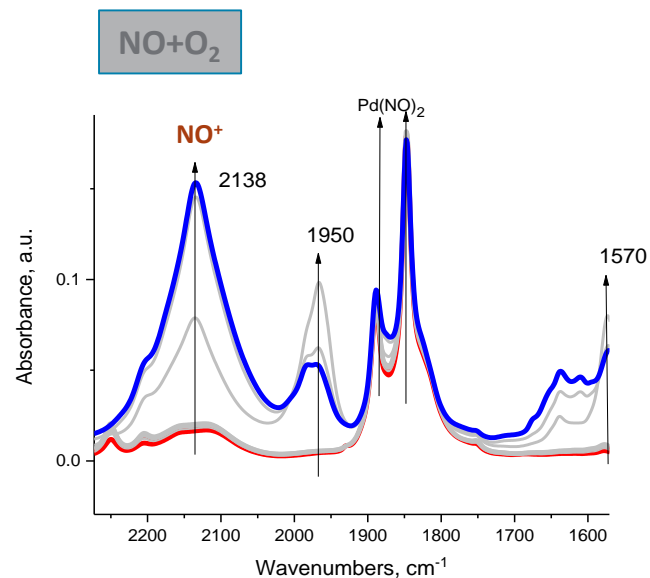
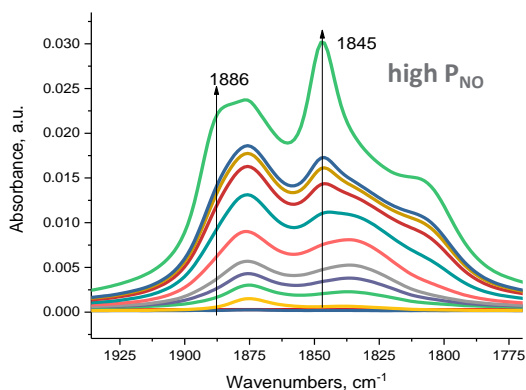
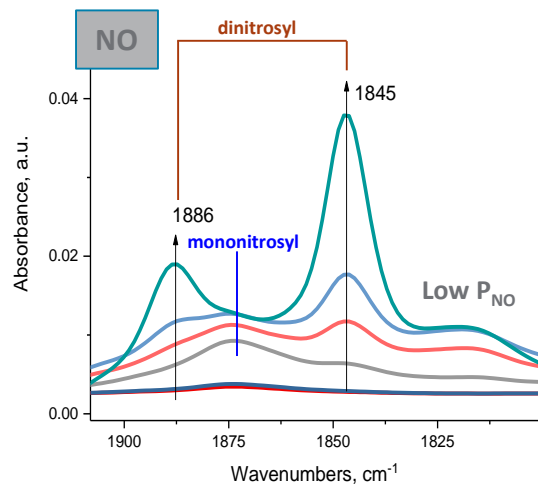


- ▶ Large BEA crystallites: higher NO_x storage capacity
- ▶ Low T NO_x release related to large number of crystal defects in nano BEA

- ▶ Decreased amount of total NO_x uptake
- ▶ HTA increases defect density, thus decreases high T and increases low T NO_x release

- ▶ No change in total NO_x uptake
- ▶ Increased defect density results in low T NO_x release

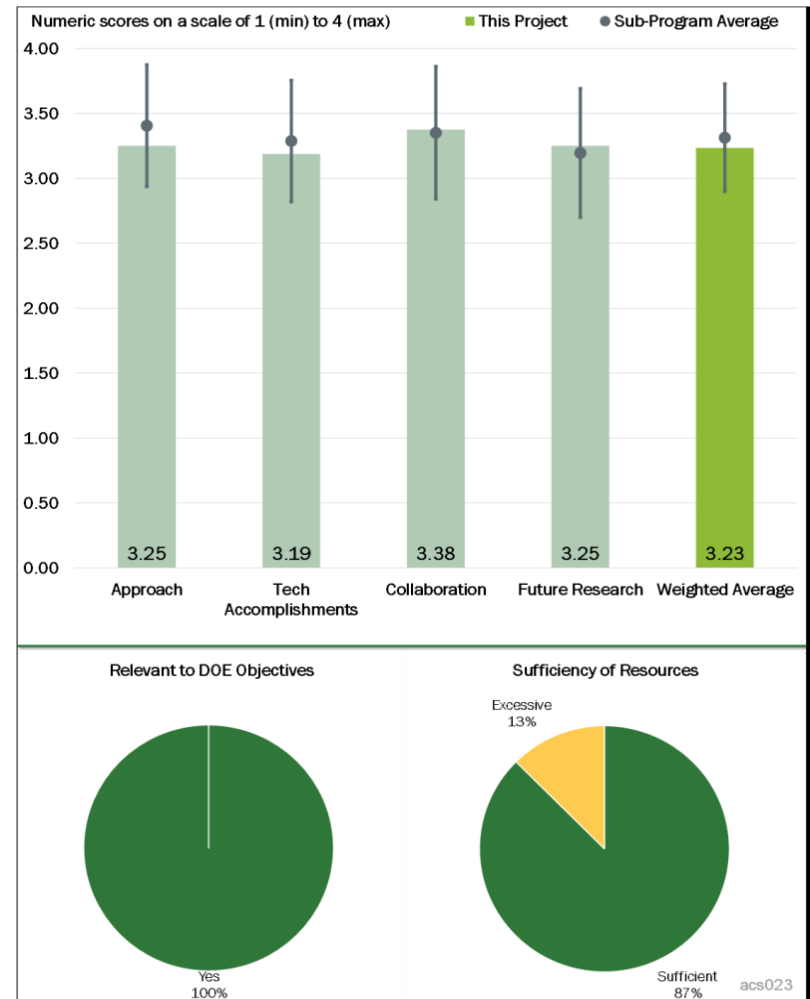
Same NO_x Chemistry on 1 wt% Pd/BEA (Si/Al=12) as SSZ-13 Except the Presence of High Temperature NO_x Release



- ▶ Two different mononitrosyl Pd(II)-NO formed upon NO adsorption
- ▶ At higher NO pressures unstable Pd(II)(NO)₂ complexes form
- ▶ NO+O₂ leads to formation of NO⁺ ions, Pd-NO complexes and N₂O₃
- ▶ CO promotes NO uptake by forming Pd(II)(NO)(CO) complexes
- ▶ Provides accurate description of Pd sites for detailed kinetic modeling

Accomplishments – Responses to Previous Years Reviewers' Comments

- ▶ Nearly all the comments from the reviewers last year were very supportive and complimentary.
- ▶ Some comments/recommendations included:
 1. It would be better to stick to two or three topics maximum as opposed to the four chosen here.
 2. examine the effects of other exhaust species on the performance of the Pd/SSZ-13 PNA catalyst, including hydrocarbons, H₂, CO₂, H₂O, and sulfur dioxide.
 3. corresponding anti-deactivation mechanism and approach should be studied with considerable urgency.
 4. how much PNNL really collaborates with ORNL on coordination of CLEERS as it seems to be solely ORNL.
 5. including an increased range of industrial partners
- ▶ PNNL response:
 1. Focuses on PNA in FY2019
 2. Study the effects of SO₂, and C₂=
 3. Understand the mechanism and evaluating mitigating approaches of crystalline beta zeolite.
 4. Assist ORNL in organizing CLEERS workshop, including organizing and leading the panel discussion, monthly teleconf calls.
 5. BASF as new partner



Collaboration and Coordination with Other Institutions

Collaborators/Coordination

- ▶ DOE Advanced Engine Crosscut Team (this group is the primary sponsor and overseer of all activities)
- ▶ CLEERS Focus Groups
- ▶ USCAR/USDRIIVE ACEC team
- ▶ 21CTP partners
- ▶ Oak Ridge National Lab: Melanie Debusk, Jim Parks, Josh Pihl, Vitaly Prikhodko, Todd Toops
- ▶ BASF: Saeed Alerasool, Pascaline Tran, Xinyi Wei, Jeff Hoke
- ▶ Cummins: Krishna Kamasamudram
- ▶ Sofia University, Bulgaria: Hristiyan A. Aleksandrov and Georgi N.Vayssilov
- ▶ University of Kansas: Franklin Tao

Acknowledgements

- ▶ DOE EERE Vehicle Technologies Program: Gurpreet Singh and Ken Howden.

Remaining Challenges and Barriers

- ▶ Long-term cyclic stability including NO_x storage capacity and release temperature.
- ▶ Performances under extreme conditions including temperatures, hydrothermal aging, exhaust gas compositions such as reducing conditions (high CO content) and presence of olefins.
- ▶ Interference with other catalysts such as DOC.

Proposed Future Work

- ▶ Evaluate PNA performances under highly reducing conditions such as high CO concentration, understand the underlying mechanisms of PNA materials degradation, e.g., possible Pd sintering, and provide guidance in mitigating the issue.
- ▶ Modification of zeolites to minimize the defect sites to improve hydrothermal stability.
- ▶ Further study the poisons of PNA materials by sulfur and HC.
- ▶ Understand the potential interference and interactions with DOC etc.

Any proposed future work is subject to change based on funding levels

- ▶ Achieved atomic Pd dispersion with modified preparation method and selection of right form of zeolites.
- ▶ Provided more accurate descriptions of Pd sites under practical conditions for simulations under CLEERS.
- ▶ Negligible sulfur effect was observed with Pd/SSZ-13.
- ▶ Understood the degradation issues under hydrothermal aging.
- ▶ Identified large crystalline BEA is a potential candidate with improved hydrothermal stability.



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Technical Backup Slides

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Pacific Northwest National Laboratory

Effect of Si/Al ratio on PNA performance:

1 wt% Pd/SSZ-13 prepared by IWI with NH_4 -SSZ-13

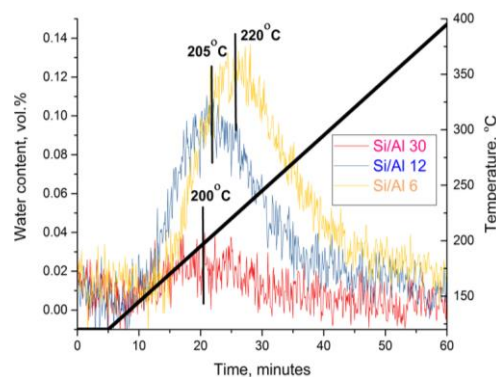


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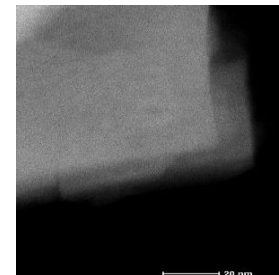
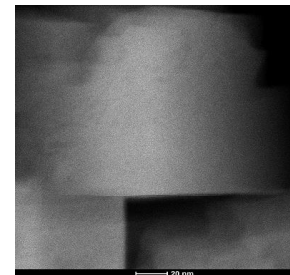
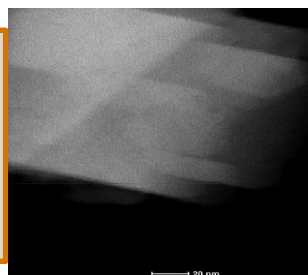
Si/Al	6	12	30
NO/Pd:	1	0.87	0.31
Storage (mg/g)	2.8	2.4	0.9

- ▶ Progressive agglomerations of Pd as Si/Al ratio increases
- ▶ PdO is not active for PNA
- ▶ Atomically dispersed Pd is the true PNA active species
- ▶ In 1 wt% Pd/SSZ-13 with Si/Al=6 potentially all Pd is atomically dispersed and this sample utilizes each Pd atom for PNA storage

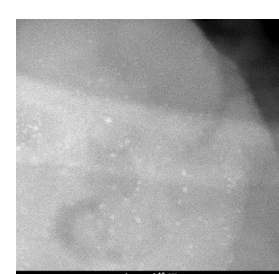
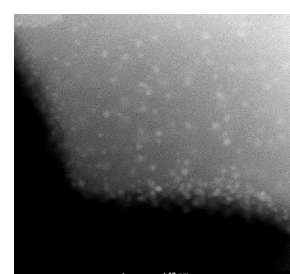
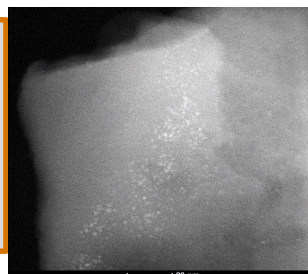


Hydrophilicity
decreases with
increasing Si/Al
ratio

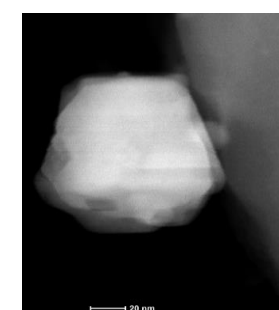
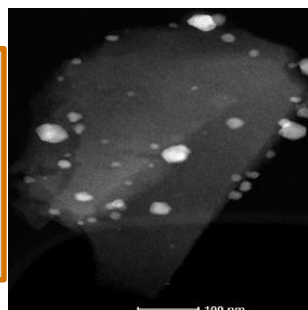
▶ Si/Al=6



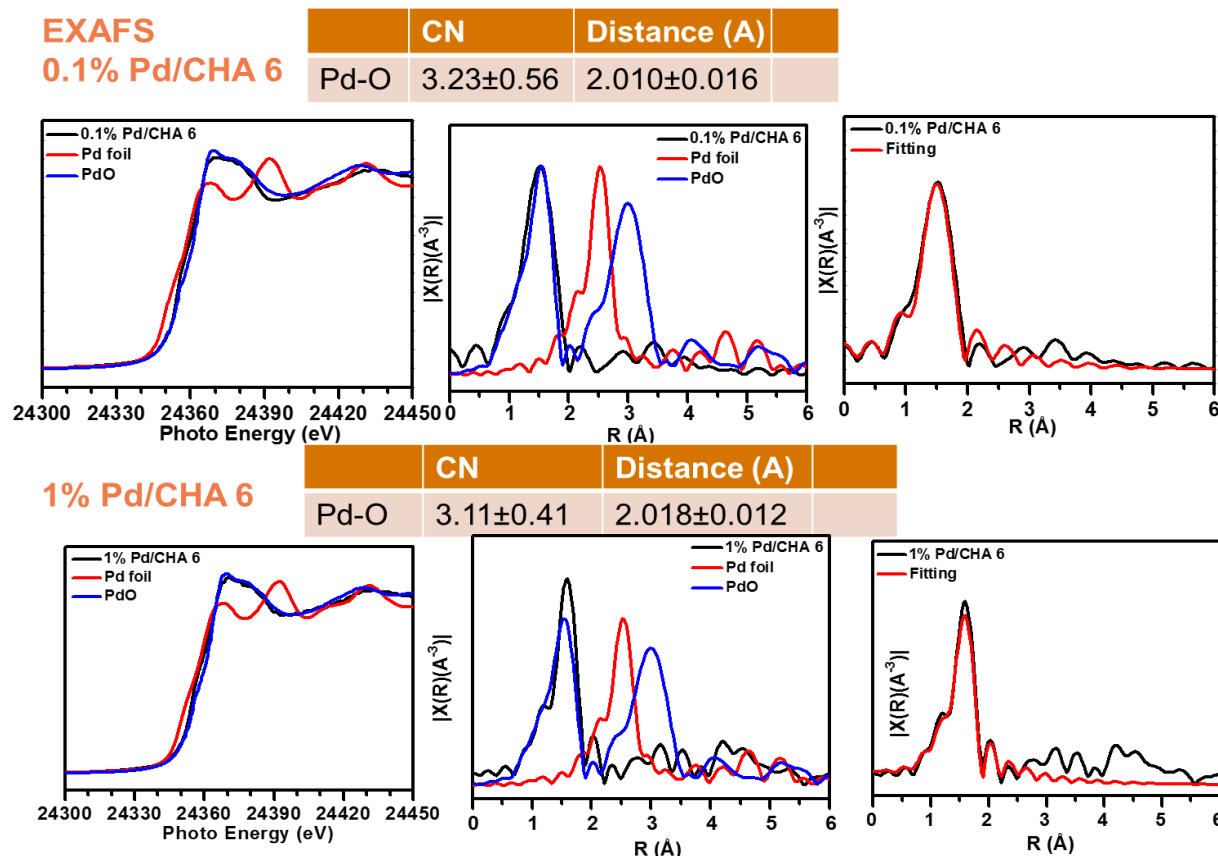
▶ Si/Al=12



▶ Si/Al=30



EXAFS of 0.1 and 1 wt% Pd/SSZ-13 (Si/Al = 6)



K.Khivantsev et. al., *Angewandte Chemie, Int.Ed.*, 2018, DOI: 10.1002/anie.201809343

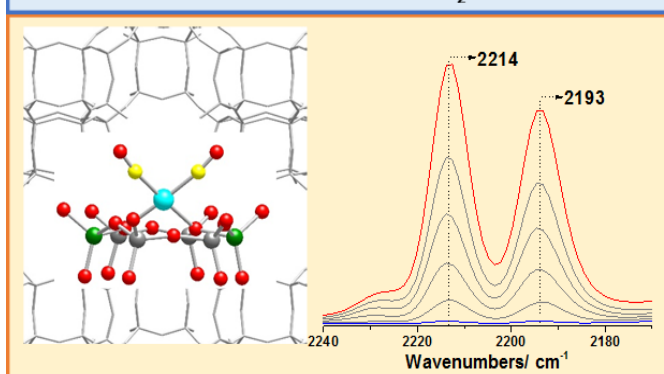
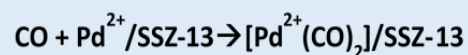
- ▶ Both 0.1 and 1 wt% Pd show no Pd-Pd contributions
- ▶ Pd is atomically dispersed, Pd₁O₍₃₋₄₎ site

Pd(II) ions are super electrophilic in SSZ-13

Atomically dispersed 1
wt% Pd/SSZ-13 (Si/Al=6)

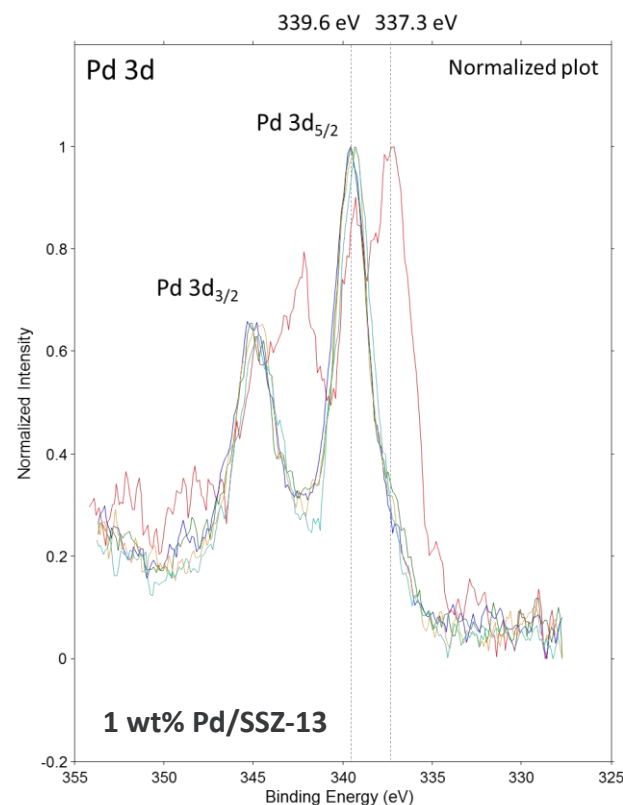


Non-classical dicarbonyl complex
form on Pd/SSZ-13



Unprecedented 2.3 eV shift in the XPS spectra
of Pd(II) upon dehydration proves
superelectrophilic nature of Pd ions in zeolite:

ion-pair/charge-transfer complex with
framework O atoms

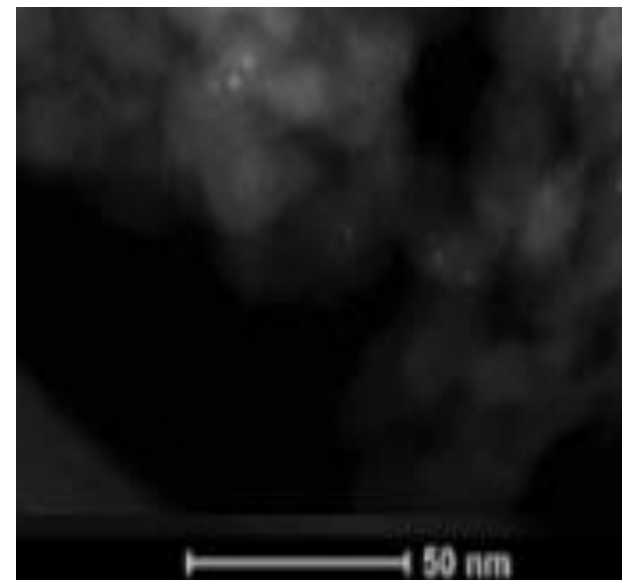
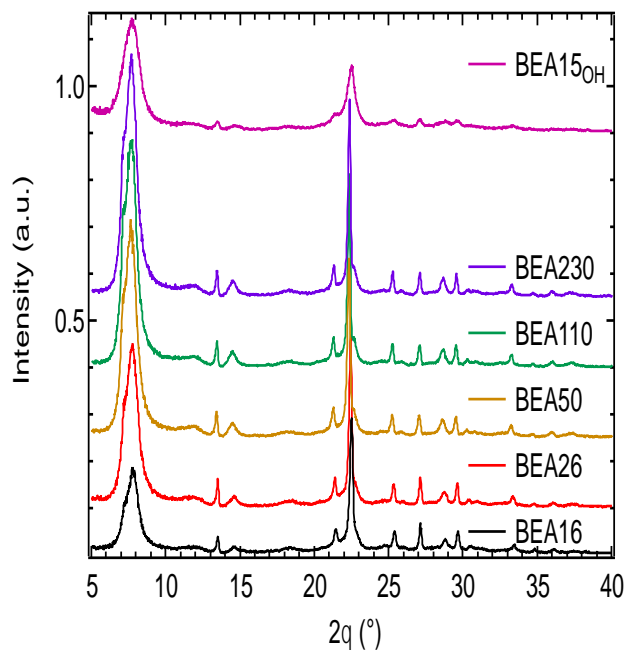
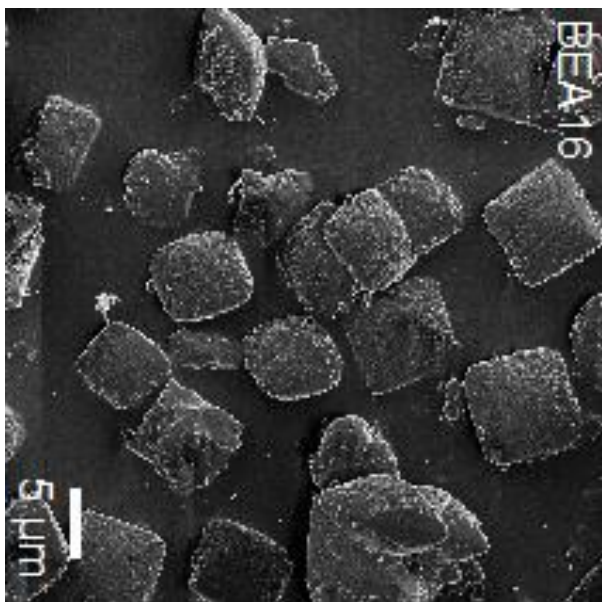


K.Khivantsev et. al., *submitted*

Two different sizes for BEA crystals with similar Si/Al 13 & 15: nanoBEA and large, defect-free, more hydrophobic BEA produced using fluoride

- ▶ In contrast to OH- medium no intercrystalline mesoporosity
- ▶ XRD shows well resolved and narrow peaks indicating high degree of order and no amorphous background.

He ion microscopy

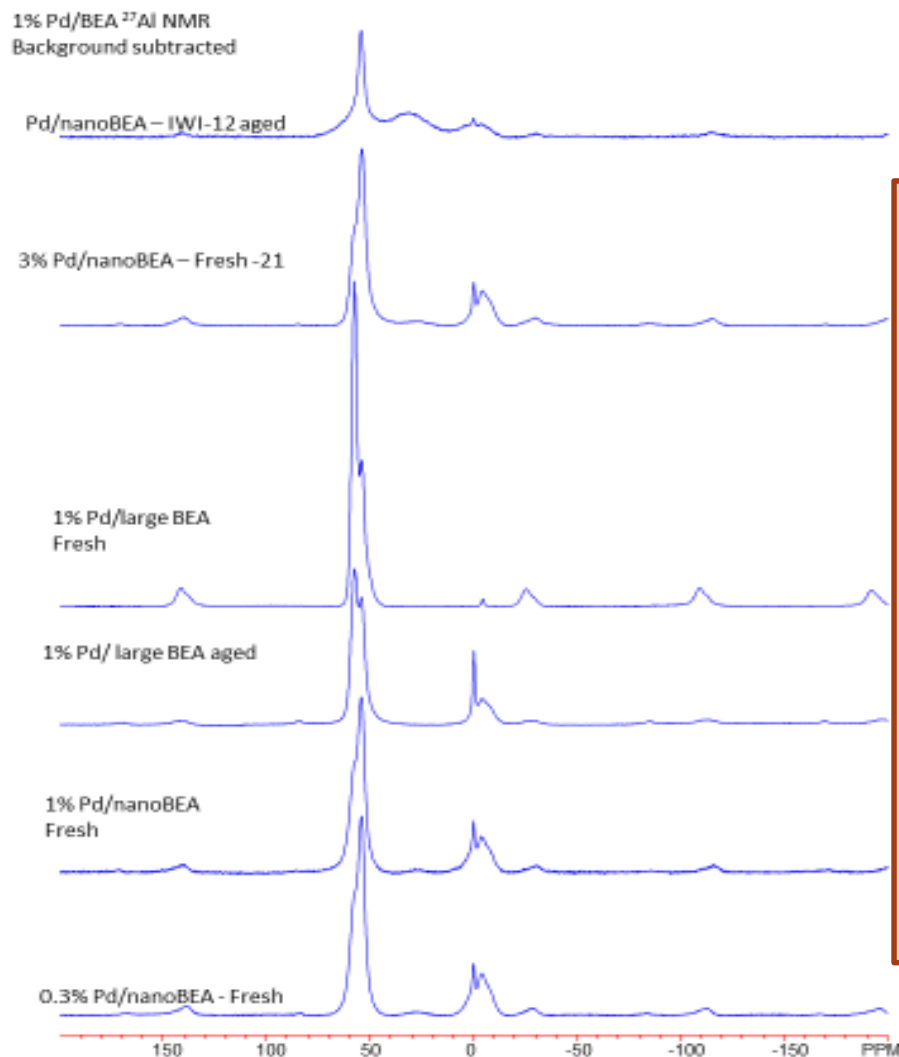


Enhanced HTA stability of large BEA crystallites: MAS Solid-state ^{27}Al NMR for BEA fresh and aged samples



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- Large BEA crystals are less defective and more hydrothermally stable
- HTA of 1 wt% Pd/nanoBEA induces a lot of dealumination
- HTA of 1 wt% Pd/large BEA induces less structural degradation
- Due to this, Pd on large BEA shows much better hydrothermal stability compared with Pd supported on regular nanosized BEA crystals